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ELECTRICALLY STIMULATED BILAYER HYDROGELS AS MUSCLES

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ABSTRACT

Muscle-like actuators have been made from bilayers of crosslinked polyacrylamide and polyacrylic acid hydrogels sandwiched between electrodes. The polyacrylic acid responds to applied positive polarity field by contracting and expelling water which is taken up by the polyacrylamide layer. Previous studies have shown that the effective swelling modulus of polyacrylamide is much lower than polyacrylic acid. Hence the polyacrylamide acts as a sponge. As the polyacrylic acid layer contracts in the x,y and z directions the polyacrylamide is also pulled in on x and y, so that the whole stack becomes narrower and expands along the z-axis. Reversing the field reverses this effect with a time constant of about 1 minute for 1 mm thick layers with a thickness change of about 10%. Linear changes up to 50% have been obtained.

Other gel actuators either transfer water across a sheet and so bend, or contract by expelling water. This new system shows a linear contraction and expansion without a volume change and so can be run (sealed) in a dry environment.

Keywords:

Hydrogels, Muscle-like actuators, polyacrylamide polyacrylic acid.

1. INTRODUCTION

There is an obvious need in robotics for synthetic actuators with properties close to those of biological muscle. These requirements could include contractions of about 50% in a time of about 1 second, a maximum stress above 200 kPa and a power density of 50 W/kg. In the absence of other convenient energy sources, the synthetic muscle should be powered electrically.

Only polymer gels seem capable of producing sufficiently large strains. There have been demonstration systems which promise to meet most of the requirements listed above, but only when powered chemically, by added solvent or a pH change^{1,2}. Outfitting a robot with a metabolic system and blood supply to provide the necessary reagents would be a major inconvenience.

There have been many studies of the electrical response of polymer gels. The archetypal system is a cross-linked hydrogel of polyacrylic acid. When a strip of gel is placed in water between two electrodes, it bends. The bending direction is dependent on the details of the experiment, whether the electrodes are touching the gel surface³ and the relationship between the gel composition and the surrounding fluid. This complexity reflects the fact that the electrical field provides an asymmetric stimulus and any differential response between the two surfaces will lead to bending.

The primary response of these gels is ionization at high pH. In the acid form, at a pH below 4, the gel is slightly swollen but it swells strongly in base, at a pH above 7. However, a number of secondary effects also lead to volume changes and will cause the gel to bend in an electrical field under the right circumstances.

We have been exploring the use of multilayer gels to produce better actuators. The aim was to produce an electrically-driven actuator that provides a linear contraction or expansion, rather than bending. It should also be able to run dry, in the sense of being sealed in a cell not much larger than the swollen gel, rather than requiring a water bath. It should also be possible to group many thin layers of gels and actuators to make a larger "muscle". Bending actuators do not lend themselves to being stacked in order to get larger forces. The underlying philosophy for our work is that the asymmetry of the field can be balanced by an asymmetry in the gel structure in order to provide a symmetric response. This response should be a shape change, rather than a volume change.

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2. GEL FORMATION

Gels stacks were made by extrusion freeform fabrication. Acrylic monomer, water and catalyst is extruded from a syringe through a fine (0.2-1 mm diameter) nozzle which writes on a heated substrate. The composition of the gel can be changed by swapping syringes or by using a Y-junction between two syringe feeds. To prevent the monomer solution from flowing off the substrate before curing, 8 wt% of fumed silica is added to the solution, to give it a toothpaste-like rheology. The solution cures to cross-linked gel by thermally activated free radical polymerization within a few minutes of being deposited on the plate. Typically 6-layer stacks were formed into bars 5 cm x 0.5 cm (wide) x 0.4 cm (thick), before swelling.

A typical stack would have a polyacrylic acid face with 1-5 (x) layers and a polyacrylamide face of (6-x) layers with a combination of dense and open-mesh layers (written as a series of spaced lines). When used, wire electrodes were usually placed between layers 1&2 and 5&6.

The system used on this work was solutions of acrylamide or acrylic acid at 2-4g/10ml of water. The cross-linking agent was methylenebisacrylamide at levels from 0.2g to 0.5 g. for the acrylamide, the initiator was potassium persulfate, 0.0025g and the accelerator was tetramethylethylenediamine (TEMED) 0.036g. For the acrylic acid, the catalyst system was a potassium persulfate (0.0114g)-potassium metabisulfite (0.0094g) redox couple. Fumed silica (2.1 g) was added and the pH adjusted to 3.8-4.0.

3. BENDING OF MULTILAYER GEL STACKS IN BASE

Initially this study sought to demonstrate very strong bending responses in six layer gel stacks with from one to five layers of polyacrylic acid gel and the remainder polyacrylamide⁴. It seemed reasonable that the acid gel would swell strongly in base, while the acrylamide would not. As a result the bars should bend with the polyacrylamide surface concave.

The results for the weight change of such bars on immersion in base are shown in figure 1. In fact relatively little bending was observed. In addition, the weight change of a bar with two polyacrylic acid layers and four polyacrylamide layers was quite comparable to that for six layers of polyacrylic acid.

The absence of bending implies that the polyacrylamide gel is relatively soft and does not constrain the polyacrylic acid layers. Similarly, little bending would be expected on heating a strip of metal with attached rubber layers. Since our experiment is being carried out in water, the polyacrylamide is soft to deformation in water with a volume change. It is not unexpectedly soft when tested in air⁴. It would also be expected that the polyacrylamide section of the bar would be extended in the length and width directions but would contract along the thickness direction. In fact the weight change shows that the polyacrylamide layer is increasing in volume and so must have a small or negative Poisson's ratio. Such effects have been described for immersed gels^{5,6}.

These observations suggested to us that the polyacrylamide layers can act as a bellows and increase or decrease in volume under the force applied by the polyacrylic acid gel. Thus it should be possible to form an electrically driven stack where contraction of a polyacrylic acid layer would drive water into an attached polyacrylamide layer, which would contract in the length and width directions but would expand in the thickness direction to accommodate the increased volume of water. A sketch of this is shown in figure 2.

4. ELECTRICALLY-DRIVEN CONTRACTION OF GEL STACKS

Initially, we built stacks of six gel layers : three of polyacrylic acid gel followed by three of polyacrylamide gel with palladium wire electrodes between layers 1&2 and 5&6. The shrinkage of these gels was studied in response to applied field.

The response of the system was made complicated by the strong dependence on the state of the gels. First the stack was swollen in dilute base to allow the acid gel to ionize fully and to swell the acrylamide gel to equilibrium. It was then washed in deionized water. The stack was then treated briefly for 5 minutes with dilute acid (0.25M HCl) to bring the acid gel close the point at which a large volume change occurs in response to a small change in the degree of ionization. From this state, a potential of 6 Volts, with the acrylic acid side positive, was applied for 12 minutes and the stack contracted by about 50% along the x and y axes. The contraction of the resulting gel is shown in figure 3. During this process, some water exuded

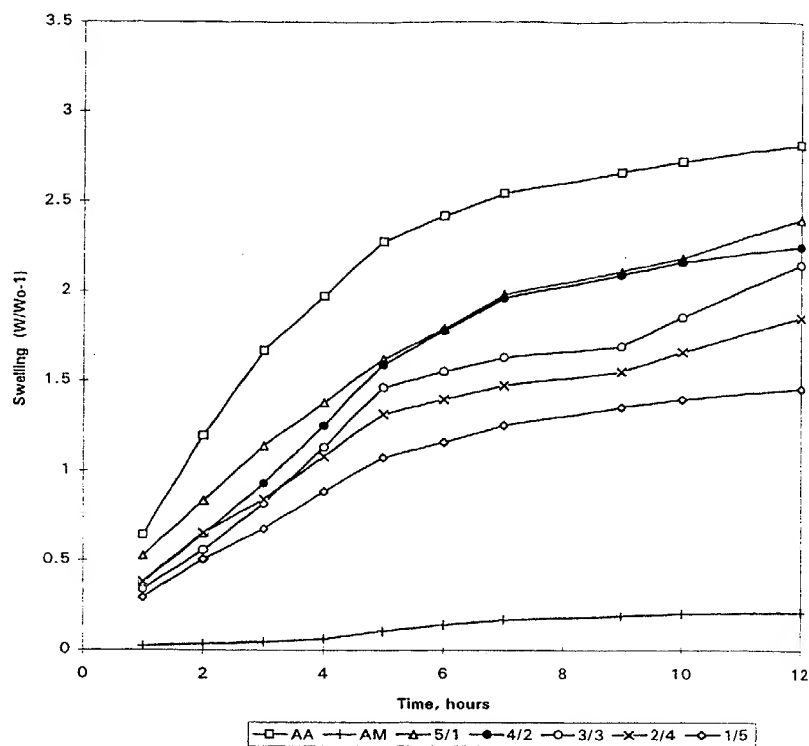


Figure 1) Swelling of multilayer stacks of acrylamide and acrylic acid gels. 0.03M monomers, 4%(vs. monomer) crosslinking. (AA: 6 layers, Acrylic acid; AM: 6 layers Acrylamide; 5/1: 5 layers AA and 1 layer AM)

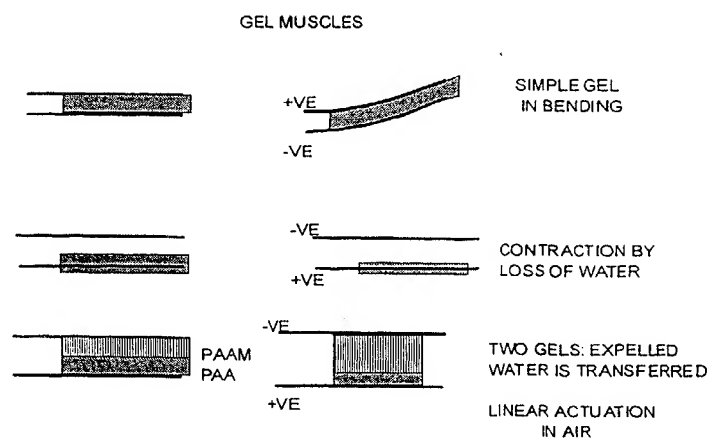


Figure 2: Sketch of response of one- and two-layer gels to an applied field. Left, no field, right, field applied.

from the system with a weight loss of 20-30%. Thus the area of the sample changed by a factor of four, the weight decreased by about 30% and the thickness must increase. The current flowing during this process was about 8 mA/cm². This system was not wholly satisfactory as there was tendency of the gel to burn around the wire electrodes and for the electrodes to pull out with these large shape changes.

An alternative system was developed with carbon foil electrodes placed above and below a gel stack. The system was taken through the cycle of swelling in base and then deswelling in acid, as before. The shape change on applying a potential was then followed by recording the deflection of a laser reflected off the surface of the stack. The results of this are shown in figure 4. It can be seen that the thickness changes by about 10% in 1 minute and the change at 3V is roughly twice that at 1.5V. We were concerned that this height change might be due to bending, rather than a thickness change. No difference was seen between height changes at the edge and center, so this is believed to be a simple thickness change, occurring as the acid gel contracts along the x-y directions and displaces water into the acrylamide gel, which expands along the z-direction. A sample was subjected to a series of 10 cycles, with current on for 1 minute, off for 1 minute, reversed for one minute then off for 1 minute, as shown in figure 5. These preliminary results show that the 10% thickness change is quite reversible.

DISCUSSION

A swollen, ionized gel is not a simple material. As made it will normally not be in swelling equilibrium with the liquid it contains. If it is allowed to equilibrate, the degree of swelling, per gram of dry gel, will depend on the crosslink density and on the pH and ionic strength of the medium. We believe that the responses of our gels can be interpreted in these terms plus the effect of applied field in lowering the pH next to the positive electrode and raising the pH next to the negative electrode. The response of a gel to applied field is strongest in the range of pH4-pH5 where the degree of swelling changes fastest with pH. This is not where the degree of ionization changes fastest with pH.

By coupling a soft neutral gel to an ionizable gel, get can obtain a linear contraction, and no volume change, with applied potential. A synthetic muscle that would change thickness, like an electrically-driven jack, seems quite feasible with this system. For a faster response, many thin layers are needed, with interleaved electrodes. The gels probably also need to be reinforced with flexible fibers to provide mechanical strength without compromising the shrinkage.

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REFERENCES

1. S. Umemoto, N. Okui and T. Sakai. in *Polymer Gels* (eds. DeRossi, D., K.Kajiwara, Osada, Y. & Yamauchi, A.) pp. 257-270 (Plenum, NY, 1991).
2. M. Suzuki. in *Polymer Gels* (eds. deRossi, D.) pp.221-236 (Plenum, New York, 1991).
3. M. Doi, M. Matsumoto and Y. Hirose, *Macromolecules* **25**, 5504-5511, 1992.
4. P. Calvert and Z. Liu, "Freeform Fabrication of Hydrogels", *Acta Materialia* **46**, 2565-2571, 1998.
5. T. Takigawa, Y. Morino, K. Urayama and T. Masuda, "Osmotic Poisson's ratio and equilibrium stress of Poly(acrylamide) gels", *Polymer Journal*. **28**, 1012-1013, 1996.
6. C. Li, Z. Hu and Y. Li, "Poisson's ratio in polymer gels near the phase-transition point", *Phys. Rev. E* **48**, pp. 603-606, 1993.

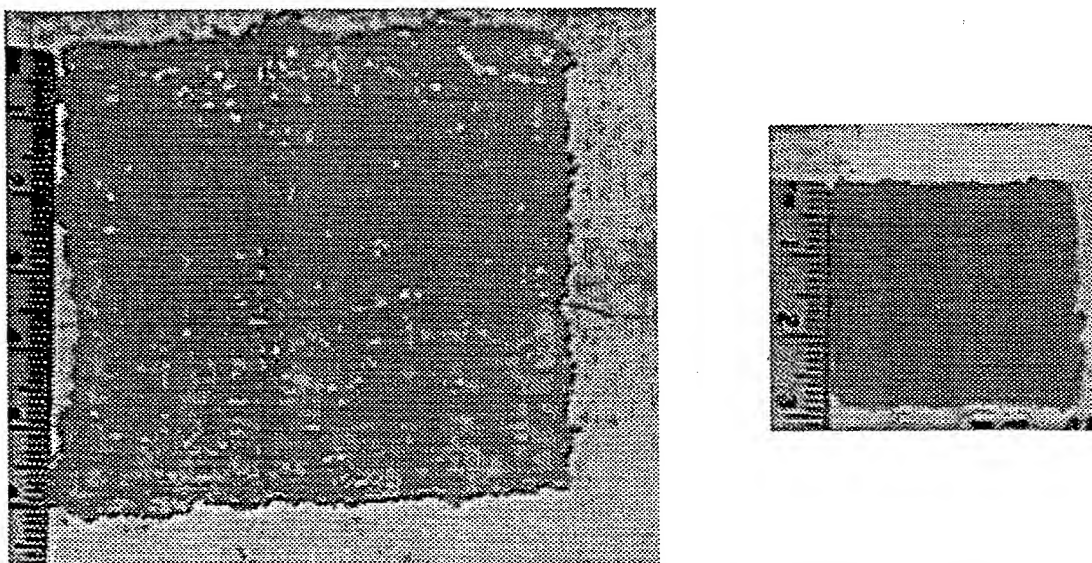


Figure 3: Gel sheet before (left) and after (right) applied potential of 6V for 12 minutes

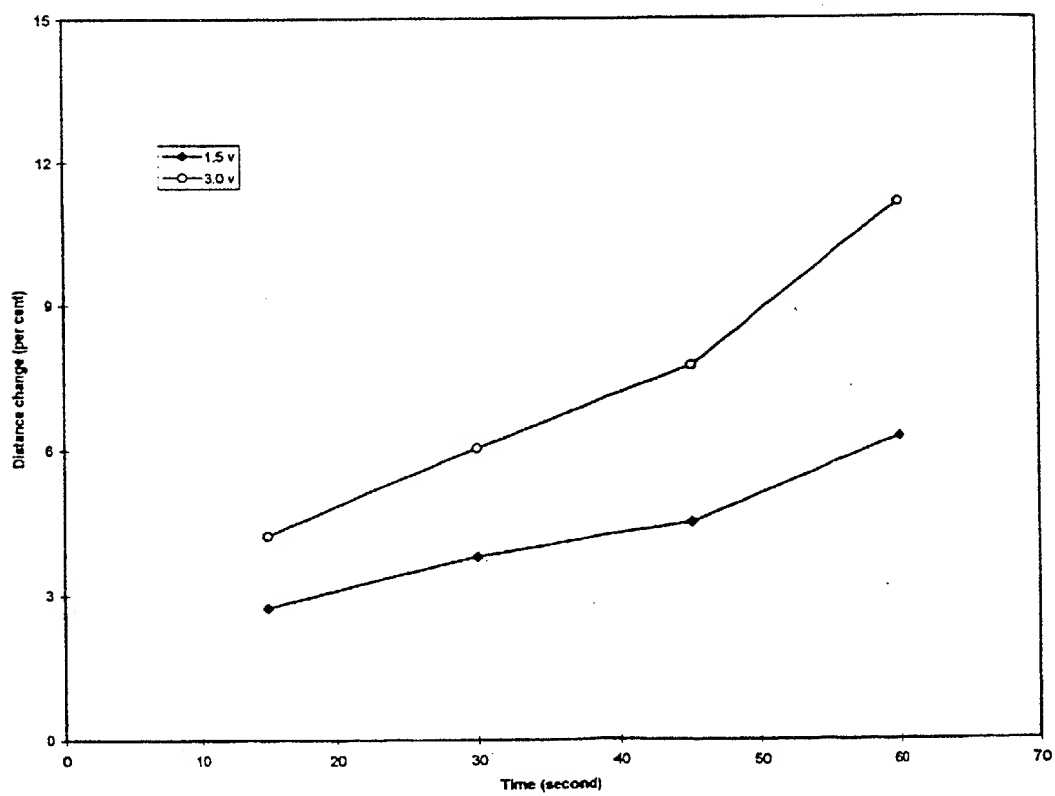


Figure 4: % thickness change in a gel stack between graphite foil electrodes.

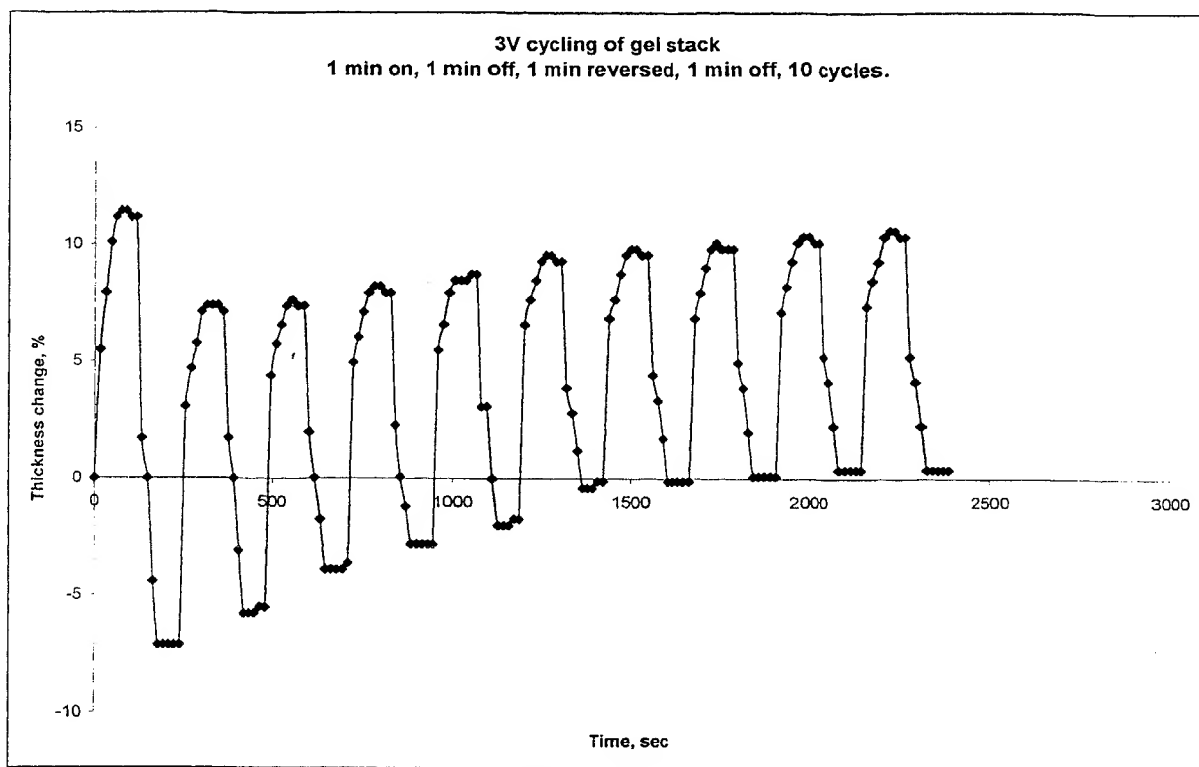


Figure 5: Cycling of a gel stack from +3V to 0V to -3V to 0V.